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CHEMISTRY AND EVOLUTION OF TITAN'S ATMOSPHERE, Darrell F. Strobel, Naval Research Laboratory, Washington, D.C. 20375

The chemistry and evolution of Titan's atmosphere is reviewed in light of the scientific findings from the Voyager Mission. It is argued that the present N_2 atmosphere may be Titan's initial atmosphere rather than photochemically derived from an original NH_3 atmosphere. The escape rate of hydrogen from Titan is controlled by photochemical production from hydrocarbons. CH_4 is irreversibly converted to less hydrogen rich hydrocarbons, which over geologic time accumulate on the surface to a layer thickness of $\sim$ 0.5 km. Magnetospheric electrons interacting with Titan's exosphere may dissociate enough N_2 into hot, escaping N atoms to remove $\sim$ 0.2 of Titan's present atmosphere over geologic time. The energy dissipation of magnetospheric electrons exceeds solar EUV energy deposition in Titan's atmosphere by an order of magnitude and is the principal driver of nitrogen photochemistry. The environmental conditions in Titan's upper atmosphere are favorable to building up complex molecules, particularly in the north polar cap region.

WHAT CONTROLS THE CO_2 CONTENT OF THE ATMOSPHERE?

Wallace S. Broecker

Our record of the CO_2 content of the atmosphere currently extends back only 40,000 years. Beyond this we can only speculate about the variations in the partial pressure of this important greenhouse gas. These speculations are based on our limited knowledge of the factors currently influencing the chemistry of the ocean (since the ocean contains about 60 times more carbon than the atmosphere, it dictates the atmosphere's CO_2 content). While these speculations suggest that the CO_2 content has very likely changed with time, they do not permit much to be said regarding the amplitude or timing of these changes. They do, however, allow the dismissal of the simplistic scenarios often encountered (i.e., there must have been more CO_2 in the atmosphere during times like the Pennsylvanian when so much organic matter was deposited or times of greater volcanicity should be times of greater atmospheric CO_2 content). The major point to be made is that the control mechanisms for ocean chemistry are largely kinetic. The O_2 and CO_2 content of the atmosphere and the pH and PO_4 content of sea water are the agents which force the output from the ocean to match the inputs to the ocean.

ANCIENT ATMOSPHERIC ARGON IN CHERTS.

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The outgassing rate of atmospheric noble gases can in principle be inferred from a knowledge of the variation of the atmospheric ($^{40}Ar/^{36}Ar$) ratio as a function of time. In an attempt to determine the composition of atmospheric argon in the past we are carrying out an analytical programme involving the analysis of argon extracted from cherts and silicified plants. The samples analysed include ones which have been subjected to neutron irradiation in order to use the ^{40}Ar-^{39}Ar technique to correct for in situ decay of ^{40}K in addition to providing chronological information. As well as attempting to determine the ($^{40}Ar/^{36}Ar$) ratio our aims have been to provide a systematic understanding of the way in which atmospheric gases are incorporated in chert and to investigate the likelihood of inferring sensible values for the isotopic composition.

In our preliminary work we have analysed twenty discrete samples from ten individual specimens. The specimens consisted of four silicified plants and two cherts with ages ranging from Permian to Eocene, and four ancient cherts from the Precambrian. The rationale behind the analysis of the recent cherts (in addition to seeking to demonstrate the presence of atmospheric argon) was to see whether they would indeed yield a sensible value for the composition of the (modern) atmosphere, or whether they would be seriously affected by such processes as mass fractionation or the incorporation of excess radiogenic argon. Clearly if it is not possible to use cherts to determine the (known) composition of today's atmosphere there is little point in making strenuous efforts to use them to determine the composition of the ancient atmosphere.

The 'recent' specimens have ages ranging from 50 Ma to 250 Ma and all contain significant amounts of dissolved argon. Concentrations of ^{36}Ar range from 7×10^{-9} ccSTP/g to 3×10^{-8} ccSTP/g. For comparison Cadogan (1977) observed a concentration of 2.5×10^{-8} ccSTP/g in Rhynie chert. The equilibrium solubility of atmospheric argon in terrestrial surface waters corresponds to concentrations roughly a factor of 100 greater than this (i.e. from 10^{-6} to 2×10^{-6} ccSTP/g). Since cherts typically contain structural and non structural water at the 1% level it seems likely that the argon we find in the cherts was originally dissolved in the ground water responsible for the silicification and was simply trapped during silicification.

The argon has been analysed during stepped heating experiments and shows a characteristic bimodal release pattern with major release (75%) at temperatures in excess of 1200°C, indicative of the fact that a major component of the gas is very strongly bound within the chert, and is not (for example) simply adsorbed from the present day atmosphere. Cadogan's Rhynie chert data shows a similar release pattern which may be a useful diagnostic feature in future attempts to identify ancient atmosphere in Precambrian samples. Estimates of diffusion coefficients and activation energies suggest that argon should be retained in cherts for times of the order of 1000 Ma or greater provided they are not subjected to temperatures in excess of 2 - 300°C. Interpretation of diffusion data in a simple minded way is clearly suspect, nevertheless the analysis does suggest, qualitatively at least, that dissolved atmospheric argon is only likely to be found in those Precambrian samples which have escaped all but the mildest metamorphism.

Neutron activation provides a means of determining concentrations of K, Ca and Cl, by way of neutron reactions which produce ^{39}Ar, ^{37}Ar and ^{38}Ar respectively. K concentrations in the modern cherts are all low, from 40 to 220 ppm. Corrections for radiogenic argon are therefore small. The ^{38}Ar data is of interest since it provides a possible way of investigating the palaeoenvironment of the samples, by way of the $Cl/^{36}Ar$ ratio. In modern sea water this ratio is around $(5 - 10)\times10^6$ at/at. In four of the samples analysed the measured ratio covers the range $(1 - 2)\times10^6$, while in the remaining two Eocene samples (a silicified peat from the Albany coal basin, and Quincyte, a dolomite replacement chert from Mehun sur Yeure, France) the ratio was much lower, 0.14×10^6 and 0.13×10^6 respectively. If the 'solubility/trapping' mechanism postulated to account for the amounts of dissolved argon is correct, one might expect a similar mechanism to operate for chlorine though possibly with somewhat different efficiency due to chemical and ionic radius differences. This being so we are led to interpret the high $Cl/^{36}Ar$ ratios as an indication of silicification under saline or marine conditions and the low ratios as an indication of freshwater conditions. This interpretation is consistent with our present knowledge of

the palaeoenvironments of the samples analysed.

The recent samples were, apart from a silicified fern stem from the Permian of Autun in France, confined to a narrow age range from 50 to 150 Ma. A global plot of all the data gave a best fit ($^{40}Ar/^{36}Ar$) ratio of 296.2 + 1.5 which is within error the same as the modern atmospheric value of 295.5. The Permian sample contained the smallest amount of gas and the ($^{40}Ar/^{36}Ar$) ratio of 293 + 14 is far too imprecise to distinguish between the modern value and a value of 294.0 + 1.5 for the Permian which is implied by Cadogan's data. While it is not possible to make any inferences about the rate of change of ($^{40}Ar/^{36}Ar$) from these measurements they are encouraging in that they appear to indicate that effects of mass fractionation or the incorporation of excess radiogenic argon are unlikely to be a major problem and provided the appropriate samples can be located there appears to be no fundamental obstacle in the way of using cherts to determine the isotopic composition of ancient atmospheric argon.

The Precambrian samples analysed in the preliminary study, a stromatolite from the Gunflint, and three black cherts (Bangemall, Hamersley and Onverwacht), gave no indication of dissolved atmospheric argon, and provided some limited chronological information only. The Gunflint sample from the Mink mountain area contained 43ppm K and based on a rather imprecise isochron had apparently been outgassed 1180 + 100 Ma ago. Three Onverwacht samples gave apparent ages close to 4000 Ma, considerably higher than the published Sm-Nd age of 3540 + 30 Ma (Hamilton et al., 1979). An examination of previously published $^{40}Ar/^{39}Ar$ ages of cherts (Alexander, 1975) revealed a similar tendency towards higher than expected ages and lead us to suspect the possibility of ^{39}Ar loss due to recoil during neutron activation. This effect has been confirmed by our most recent experiments in which samples of Gunflint from the Schreiber Beach locality were irradiated in evacuated quartz ampoules. Analysis of the argon in the ampoules indicated that around 12% of the ^{39}Ar was lost from the samples during irradiation.

In this most recent study seven samples of Gunflint have so far been analysed, two unirradiated and five irradiated. Stepped heating of the unirradiated samples revealed the 'diagnostic' high temperature release of ^{36}Ar and a concentration of around $4x10^{-9}$ ccSTP/g. Because of recoil loss it is clearly not meaningful to attempt to interpret stepped heating analyses of irradiated samples. Potentially the only meaningful data to use in isotope mixing diagrams (in order to separate radiogenic and atmospheric ^{40}Ar) are 'total gas' ratios or possibly 'total gas' less a (small) correction for low temperature release of modern air argon. Unfortunately the data so far obtained does not indicate a simple binary mixture of radiogenic and atmospheric. Two samples from the same chert cobble show clear indication of excess argon (high $^{40}Ar/^{36}Ar$ ratio). Excess argon is less evident in the two unirradiated samples and the other three irradiated samples, nevertheless it is not possible to infer a unique age and $^{40}Ar/^{36}Ar$ ratio. Based on the samples with the least evidence of excess argon we can infer an $^{40}Ar/^{36}Ar$ ratio based on an assumed age for the Gunflint. The ratio inferred is in the range 296 (i.e. modern), for an assumed age of 1900 Ma, to 260, for an assumed age of 2200 Ma. These values are only consistent with low rates of outgassing of ^{40}Ar over the past 2000 Ma, viz. $<3.3x10^5$ atoms/cm2/sec. Cadogan's data on Rhynie chert corresponds to a mean outgassing rate of $(2.5 + 1.0)x10^5$ atoms/cm2/sec over the past 400 Ma. Until the source of excess argon in the Gunflint samples is isolated the calculated ratios can only be regarded as upper limits. Work is continuing on this problem.

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ESCAPE OF NITROGEN FROM THE MARTIAN ATMOSPHERE, J.L. Fox, Center for Astrophysics, Cambridge, Mass. 02138

The notion that substantial quantities of nitrogen have escaped from Mars was introduced by Brinkman[1] who considered the role of photodissociation in producing nitrogen atoms with energies exceeding the escape energy, about 1.72 eV for ^{14}N. Support for this idea was provided by the Viking mass spectrometers, which recorded an anomalous $^{15}N/^{14}N$ ratio, 1.62 $\pm$ .16 times the terrestrial value[2]. Subsequent models have considered other methods for producing energetic nitrogen including dissociative recombination of N_2^+ [3] photoelectron impact dissociation[4,5] and chemical reactions[6]. The computed rates for dissociative recombination of N_2^+ and of the reaction, $N_2^+ + O \rightarrow NO^+ + N$, depend on model N_2^+ densities which were not measured by Viking. We have refined our model to include better estimates of the N_2^+ densities from models which reflect the improved understanding of ion chemistry in CO_2 atmospheres obtained from Pioneer Venus[7,8]. In particular, the reaction $O^+(^2D) + N_2 \rightarrow O + N_2^+$ has been measured recently[9,10] and we have found it to be a major source of N_2^+ above the exobase on Mars.

Dissociative recombination produces an escape flux of 3×10^5 cm^{-2} s^{-1} and is the major source of escaping ^{14}N atoms. The escape rates for ^{15}N and ^{14}N in dissociative recombination differ substantially for ground state N_2^+ [11]. This effect will be mitigated for ions in excited vibrational levels. We have modeled the vibrational distribution of N_2^+ at the Martian exobase in order to determine the ^{15}N-^{14}N fractionation due to dissociative recombination. At 200 km, 40% of the N_2^+ ions are found to be vibrationally excited.

Photodissociation of N_2 contributes an escape flux of about 1×10^5 cm^{-2} s^{-1}. Other processes bring the total escape flux to about 5.6×10^5 cm^{-2} s^{-1}.

Fanale et al.[12] have constructed a model of the regolith-atmosphere-polar cap system in which oscillations in the obliquity of the planet, and therefore in the insolation produce periodic changes in the CO_2 pressure of the atmosphere. Pressure variations will affect the escape flux of nitrogen since the pressure determines the altitude of the exobase and the fraction of N_2 found there. We have incorporated these effects into our model and have found that the net escape rate is reduced compared to the average pressure model. For the basalt regolith, we obtain an initial $^{15}N/^{14}N$ ratio of 2.74 and an initial column density of 9.7×10^{22} cm^{-2}. For the nontronite regolith, the isotope ratio is 1.54 and the initial reservoir is 4.0×10^{22} cm^{-2}. Our model shows that a regolith material with adsorptive properties intermediate between basalt and nontronite will yield an appropriate $^{15}N/^{14}N$ ratio and total C/N ratio.

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POST-HADEAN ATMOSPHERE-HYDROSPHERE

Veizer, J.

GEOLOGIC BUFFERING OF THE HYDROSPHERE-ATMOSPHERE SYSTEM IN POST-HADEAN TIMES. J. Veizer, University of Ottawa, Canada K1N 6N5.

The kinetic steady state, buffering the composition of the present day oceans, is controlled by the following fluxes: (a) continental river discharge-F_C; (b) interaction between seawater and basalts of the oceanic crust predominantly, but not exclusively, in hydrothermal cells on mid-oceanic ridges-F_M; and (c) eflux via, and interaction with, sediments-F_S. Today, despite claims to the contrary, F_C likely outweighs F_M as the most important controlling factor of seawater composition. This is well demonstrated for tracers with differing signatures for these two fluxes. For example, the $^{87}Sr/^{86}Sr$ of F_C is 0.711 and of F_M is 0.703. Thus, a relative F_C:F_M intensity of $\sim$4.1 is required to produce the seawater ratio of 0.709. In geological past the intensity of F_C was proportional to the size of the continents, whereas that of F_M to the terrestrial heat flow. Consequently, the relative F_C:F_M intensities varied during terrestrial evolution, with the early stages being dominated by F_M and the subsequent evolution by F_C. Sr isotope data suggest that the crossover interval between a mantle (F_M) and continentally (F_C) dominated steady states was the late Archean-early Proterozoic period. Such an evolving scenario can explain the observed chemical (Fe, Fe^{2+}/Fe^{3+}, Mn, Ba, Sr ?) and isotopic ($^{87}Sr/^{86}Sr$, $\delta^{34}S$, $\delta^{18}O$) secular trends observed for chemical sediments. Furthermore, the observed sedimentological (e.g. Archean volcaniclastics vs. Proterozoic shelf sequences), geological (greenstones vs mobile belts) and metallogenetic (base metals; Fe, U, Au ores) patterns are entirely consistent with this outline.

The recent discoveries of direct evidence for existence of life since at least 3.5 Ga ago, coupled with the modern type carbon isotope record, attest to the great antiquity of life and possibly oxygen generating photosynthesis. Thus the emergence of the highly oxygenated atmosphere at $\sim$2.0 Ga ago may be a consequence of the diminishing effectiveness of oxygen sinks (reduced gases, Fe, Mn) due to declining F_M. This is in contrast to conventional explanation, which relates the event to the emergence and rapid evolution of oxygen generating biota during the early Proterozoic.

In addition to the first order evolution of the hydrosphere-atmosphere, from an F_M dominated to the F_C dominated system, second order perturbations ($\lesssim 10^7$-10^8 a) are being established for the Phanerozoic. The covariance of seawater $^{87}Sr/^{86}Sr$, $\delta^{13}C_{bicarbonate}$, $\delta^{34}S_{sulfate}$ and sea level curves provides the first direct evidence for interactions of organic and inorganic cycles on geological time scales. Although a unifying model integrating all these parameters is not yet available, the results strongly suggest that this coupling is the real controlling factor of oxygen atmospheric levels.

Seawater is a medium which integrates and records global

responses to evolution and perturbations of the past geological steady states. This record, inscribed in chemical sediments, deserves attention commensurate with its potential and significance.

What are the volatiles like inside the earth?

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If we start with the premise that the carrier of volatiles to the accumulating earth was similar to C-1 carbonaceous chondrites, then the determination of the distribution of volatiles in the earth can be made based on measurements made at the earth's surface. Heat flow measurements, Nd, Sr and Pb isotope systematics, and radiogenic and stable isotopic abundances of some of the rare gases combined with the oxidation state of mantle-derived rocks yield information for a moderately self-consistent picture of the rare gas, water and carbon content of the earth's interior.